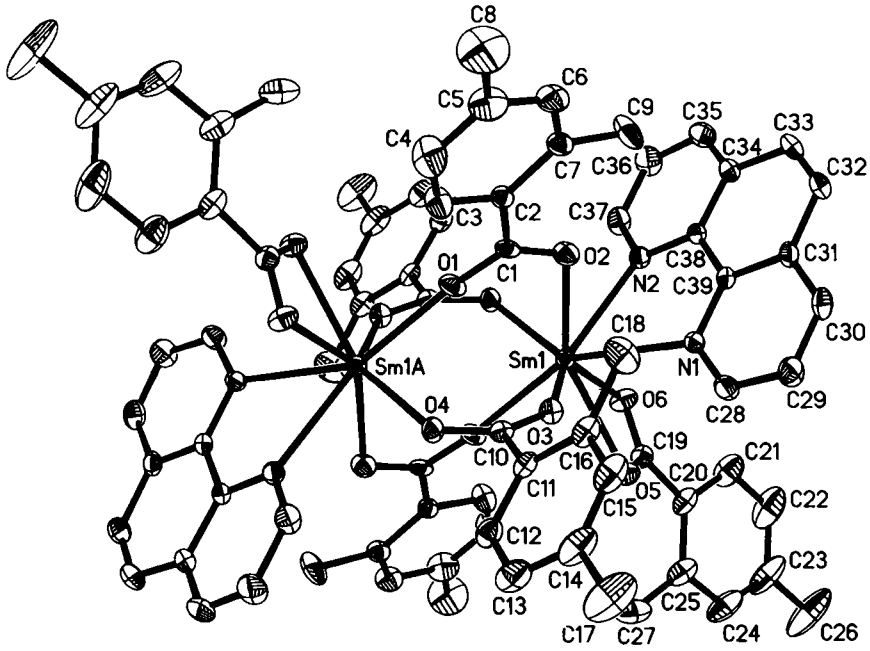
Crystal structure of bis(1,10-phenanthroline-*N*,*N*′)bis(2,4-dimethylbenzoato-*O*,*O*′)tetrakis(μ-2,4-dimethylbenzoato-*O*,*O*′)disamarium(III), $Sm_2(C_9H_9O_2)_6(C_{12}H_8N_2)_2$

T.-T. Zhang, X. Li* and Y.-L. Ju

Capital Normal University, Department of Chemistry, Beijing, 100037 P. R. China

Received October 19, 2005, accepted and available on-line December 4, 2005; CCDC no. 1267/1669



Abstract

$C_{78}H_{70}N_4O_{12}Sm_2$, monoclinic, *C*12/*c*1 (no. 15), *a* = 27.523(3) Å, *b* = 15.699(2) Å, *c* = 16.048(2) Å, *β* = 101.123(2)°, *V* = 6803.7 Å^3, *Z* = 4, $R_{gt}(F)$ = 0.026, $wR_{ref}(F^2)$ = 0.063, *T* = 294 K.

Source of material

0.5 mmol 2,4-dimethylbenzoic acid and 0.35 mmol 1,10-phenanthroline were dissolved in 7 ml distilled water. The pH value was adjusted to about 6-7 with 2 M NaOH solution. Then 0.35 mmol $SmCl_3 \cdot 6H_2O$ dissolved in 3 ml distilled water were added. The mixture was placed in a Teflon-lined stainless vessel (25 ml). The vessel was sealed and heated at 160 °C for 24 h under autogenous pressure and then cooled down to room temperature. After being filtered, the product was washed with ethanol and then dried under ambient. Column-like crystal was collected.

Discussion

Like other lanthanide carboxylate complexes containing 1,10-phenanthroline (phen) or 2,2′-bipyridine, the title complex is also a dimer with an inversion center. The two central Sm(III) ions are bridged by four carboxylate groups with Sm···Sm distance of 4.120 Å. In addition, each Sm(III) ion is chelated by one carboxylate group and one phen molecule. The coordination number of Sm(III) ion is eight, including six O atoms from carboxylate groups and two N atoms from phen ligand. They adopt a distorted square antiprism, the four apical positions of the upper square are occupied by O1A, O2, O3, and O4A, and those of the lower square by O5, O6, N1, and N2 with mean deviations of 0.056 Å and 0.209 Å between the two squares, respectively. The dihedral angle between the two squares is 7.4°.

The title molecule structure is similar to that of Eu_2(3,4-dimethylbenzoate)$_6$(phen)$_2$ [1]. However, it is different from terbium 2-methylbenzoato complex with phen, $[Tb(CH_3C_6H_4COO)_3(C_{12}H_8N_2)]_2$, in which two crystallographically different binuclear molecules exist [2]. It is also unlike dysprosium 4-methylbenzoato complex with phen, $[Dy(CH_3C_6H_4COO)_3(C_{12}H_8N_2)]_2$, which contains two different binuclear molecules having two different coordination modes of 4-methylbenzoato groups [3]. Carboxylate groups of 2,4-dimethylbenzoic acid adopt bidentate bridging and bidentate chelating modes. The distances between Sm and O atoms from bridged carboxylato groups range from 2.353(2) Å to 2.428(2) Å with an average distance of 2.389 Å. The distances between Sm and O atoms from chelated carboxylate groups are 2.427(2) Å and 2.513(2) Å, respectively, with an average distance of 2.4705 Å. The Sm—N bond lengths are 2.616(2) Å and 2.639(2) Å, respectively and the N–Sm–N angle is 62.23(7)°.

* Correspondence author (e-mail: xiali@mail.cnu.edu.cn)

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.10 × 0.16 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	17.76 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18960, 6951
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5489
$N(param)_{refined}$:	439
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	8*f*	0.1093	0.8077	–0.1113	0.057
H(4)	8*f*	0.0289	0.8541	–0.1514	0.077
H(6)	8*f*	0.0715	1.0882	–0.0764	0.056
H(8A)	8*f*	–0.0289	0.9779	–0.1875	0.148
H(8B)	8*f*	–0.0122	1.0670	–0.1481	0.148
H(8C)	8*f*	–0.0281	0.9952	–0.0910	0.148
H(9A)	8*f*	0.1502	1.1286	–0.0301	0.087
H(9B)	8*f*	0.1930	1.0718	–0.0516	0.087
H(9C)	8*f*	0.1773	1.0631	0.0369	0.087
H(12)	8*f*	0.1476	0.5966	0.1722	0.047
H(13)	8*f*	0.0959	0.5827	0.2693	0.066
H(15)	8*f*	0.0789	0.8342	0.2694	0.065
H(17A)	8*f*	0.0677	0.7127	0.4017	0.137
H(17B)	8*f*	0.0371	0.6424	0.3451	0.137
H(17C)	8*f*	0.0220	0.7384	0.3319	0.137
H(18A)	8*f*	0.1106	0.8945	0.1089	0.091
H(18B)	8*f*	0.1665	0.8910	0.1534	0.091
H(18C)	8*f*	0.1269	0.9269	0.2025	0.091
H(21)	8*f*	0.4412	0.9268	0.2618	0.075
H(22)	8*f*	0.5070	0.9321	0.3758	0.103
H(24)	8*f*	0.4649	0.7115	0.4595	0.081
H(26A)	8*f*	0.5402	0.7716	0.5325	0.190
H(26B)	8*f*	0.5332	0.8702	0.5401	0.190
H(26C)	8*f*	0.5669	0.8342	0.4798	0.190
H(27A)	8*f*	0.4004	0.6306	0.3867	0.099
H(27B)	8*f*	0.3832	0.6479	0.2892	0.099
H(27C)	8*f*	0.3543	0.6887	0.3543	0.099
H(28)	8*f*	0.2574	0.8910	0.2716	0.050
H(29)	8*f*	0.2249	0.9968	0.3443	0.059
H(30)	8*f*	0.2206	1.1342	0.2933	0.052
H(32)	8*f*	0.2426	1.2390	0.1873	0.051
H(33)	8*f*	0.2825	1.2680	0.0818	0.056
H(35)	8*f*	0.3337	1.2150	–0.0260	0.061
H(36)	8*f*	0.3705	1.1026	–0.0820	0.065
H(37)	8*f*	0.3606	0.9662	–0.0344	0.051

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	8*f*	0.290196(5)	0.838931(9)	0.079137(9)	0.02348(8)	0.01991(8)	0.02316(8)	0.00161(6)	0.00703(6)	–0.00008(6)
O(1)	8*f*	0.19946(8)	0.8079(1)	–0.0589(1)	0.050(1)	0.026(1)	0.041(1)	0.013(1)	0.019(1)	0.005(1)
O(2)	8*f*	0.22290(8)	0.9279(1)	0.0071(1)	0.030(1)	0.033(1)	0.045(1)	0.004(1)	–0.000(1)	0.004(1)
O(3)	8*f*	0.21936(7)	0.7834(1)	0.1283(1)	0.026(1)	0.034(1)	0.034(1)	–0.0021(9)	0.0109(9)	–0.0033(9)
O(4)	8*f*	0.18245(8)	0.6741(1)	0.0518(1)	0.045(1)	0.031(1)	0.029(1)	–0.005(1)	0.016(1)	–0.0049(9)
O(5)	8*f*	0.32773(8)	0.7898(1)	0.2265(1)	0.028(1)	0.044(1)	0.036(1)	–0.000(1)	0.004(1)	0.007(1)
O(6)	8*f*	0.37605(8)	0.8523(1)	0.1503(1)	0.033(1)	0.054(2)	0.033(1)	–0.002(1)	0.005(1)	0.010(1)
N(1)	8*f*	0.27567(9)	0.9609(2)	0.1827(2)	0.042(2)	0.024(1)	0.025(1)	–0.000(1)	0.011(1)	–0.001(1)
N(2)	8*f*	0.32039(9)	0.9935(2)	0.0493(2)	0.032(1)	0.029(1)	0.028(1)	–0.004(1)	0.010(1)	–0.001(1)
C(1)	8*f*	0.1906(1)	0.8835(2)	–0.0387(2)	0.036(2)	0.023(2)	0.028(2)	0.006(1)	0.016(1)	0.009(1)
C(2)	8*f*	0.1397(1)	0.9199(2)	–0.0684(2)	0.027(2)	0.026(2)	0.029(2)	0.002(1)	0.006(1)	0.000(1)
C(3)	8*f*	0.1019(1)	0.8646(2)	–0.1036(2)	0.039(2)	0.039(2)	0.063(2)	–0.001(2)	0.006(2)	–0.009(2)
C(4)	8*f*	0.0535(1)	0.8923(3)	–0.1273(3)	0.030(2)	0.070(3)	0.089(3)	–0.011(2)	0.003(2)	–0.014(3)
C(5)	8*f*	0.0415(1)	0.9756(3)	–0.1157(3)	0.031(2)	0.072(3)	0.069(3)	0.012(2)	0.007(2)	0.008(2)
C(6)	8*f*	0.0794(1)	1.0313(2)	–0.0827(2)	0.039(2)	0.045(2)	0.054(2)	0.019(2)	0.008(2)	0.004(2)
C(7)	8*f*	0.1285(1)	1.0063(2)	–0.0584(2)	0.033(2)	0.031(2)	0.037(2)	0.008(1)	0.007(1)	0.003(1)
C(8)	8*f*	–0.0118(2)	1.0068(4)	–0.1376(4)	0.036(2)	0.120(5)	0.135(5)	0.027(3)	0.003(3)	0.004(4)
C(9)	8*f*	0.1656(1)	1.0735(2)	–0.0226(3)	0.052(2)	0.028(2)	0.091(3)	0.008(2)	0.006(2)	–0.013(2)
C(10)	8*f*	0.1856(1)	0.7286(2)	0.1108(2)	0.025(2)	0.029(2)	0.027(2)	0.005(1)	0.008(1)	0.003(1)
C(11)	8*f*	0.1473(1)	0.7244(2)	0.1663(2)	0.026(2)	0.044(2)	0.022(2)	–0.004(1)	0.004(1)	–0.002(1)
C(12)	8*f*	0.1348(1)	0.6452(2)	0.1932(2)	0.038(2)	0.050(2)	0.031(2)	–0.010(2)	0.010(2)	–0.003(2)
C(13)	8*f*	0.1033(1)	0.6365(3)	0.2510(2)	0.047(2)	0.076(3)	0.042(2)	–0.022(2)	0.011(2)	0.009(2)
C(14)	8*f*	0.0830(1)	0.7087(3)	0.2813(2)	0.034(2)	0.102(4)	0.037(2)	–0.002(2)	0.016(2)	0.002(2)
C(15)	8*f*	0.0937(1)	0.7863(3)	0.2510(2)	0.039(2)	0.086(3)	0.040(2)	0.013(2)	0.015(2)	–0.009(2)
C(16)	8*f*	0.1255(1)	0.7979(2)	0.1941(2)	0.028(2)	0.055(2)	0.032(2)	0.005(2)	0.007(1)	–0.004(2)
C(17)	8*f*	0.0493(2)	0.6997(4)	0.3460(3)	0.063(3)	0.165(5)	0.059(3)	0.001(3)	0.044(2)	0.009(3)
C(18)	8*f*	0.1330(1)	0.8854(3)	0.1618(3)	0.054(3)	0.052(3)	0.082(3)	0.015(2)	0.027(2)	–0.005(2)
C(19)	8*f*	0.3693(1)	0.8180(2)	0.2191(2)	0.029(2)	0.035(2)	0.032(2)	0.005(1)	0.003(1)	–0.002(1)
C(20)	8*f*	0.4125(1)	0.8153(2)	0.2924(2)	0.028(2)	0.062(2)	0.029(2)	0.005(2)	0.006(1)	–0.004(2)
C(21)	8*f*	0.4456(1)	0.8831(3)	0.3017(2)	0.045(2)	0.092(3)	0.048(2)	–0.017(2)	0.005(2)	–0.003(2)
C(22)	8*f*	0.4853(2)	0.8861(4)	0.3700(3)	0.048(3)	0.147(5)	0.061(3)	–0.038(3)	0.004(2)	–0.020(3)
C(23)	8*f*	0.4927(2)	0.8214(4)	0.4293(3)	0.036(2)	0.169(6)	0.034(2)	0.003(3)	0.004(2)	–0.002(3)
C(24)	8*f*	0.4600(2)	0.7549(3)	0.4194(2)	0.040(2)	0.126(4)	0.037(2)	0.023(3)	0.005(2)	0.011(2)
C(25)	8*f*	0.4195(1)	0.7488(3)	0.3521(2)	0.038(2)	0.077(3)	0.034(2)	0.019(2)	0.010(2)	0.006(2)
C(26)	8*f*	0.5374(2)	0.8246(5)	0.5022(3)	0.048(3)	0.28(1)	0.044(3)	–0.008(4)	–0.007(2)	–0.007(4)
C(27)	8*f*	0.3864(2)	0.6721(3)	0.3449(3)	0.068(3)	0.069(3)	0.061(3)	0.019(2)	0.011(2)	0.028(2)
C(28)	8*f*	0.2571(1)	0.9466(2)	0.2514(2)	0.062(2)	0.031(2)	0.038(2)	–0.002(2)	0.023(2)	–0.000(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(29)	8*f*	0.2369(1)	1.0101(2)	0.2955(2)	0.071(3)	0.046(2)	0.040(2)	–0.002(2)	0.032(2)	–0.006(2)
C(30)	8*f*	0.2351(1)	1.0914(2)	0.2662(2)	0.050(2)	0.041(2)	0.040(2)	0.002(2)	0.016(2)	–0.017(2)
C(31)	8*f*	0.2554(1)	1.1102(2)	0.1944(2)	0.038(2)	0.029(2)	0.031(2)	–0.001(1)	0.001(1)	–0.009(1)
C(32)	8*f*	0.2577(1)	1.1949(2)	0.1630(2)	0.056(2)	0.026(2)	0.044(2)	0.007(2)	0.008(2)	–0.008(2)
C(33)	8*f*	0.2809(1)	1.2120(2)	0.1000(2)	0.068(3)	0.021(2)	0.051(2)	0.002(2)	0.008(2)	–0.004(2)
C(34)	8*f*	0.3042(1)	1.1448(2)	0.0585(2)	0.049(2)	0.026(2)	0.035(2)	–0.006(1)	0.004(2)	–0.002(1)
C(35)	8*f*	0.3307(2)	1.1599(2)	–0.0062(2)	0.073(3)	0.033(2)	0.049(2)	–0.017(2)	0.015(2)	0.008(2)
C(36)	8*f*	0.3521(2)	1.0934(2)	–0.0400(2)	0.074(3)	0.048(2)	0.050(2)	–0.020(2)	0.034(2)	–0.000(2)
C(37)	8*f*	0.3460(1)	1.0111(2)	–0.0106(2)	0.048(2)	0.042(2)	0.043(2)	–0.009(2)	0.023(2)	–0.007(2)
C(38)	8*f*	0.3003(1)	1.0605(2)	0.0854(2)	0.033(2)	0.023(2)	0.027(2)	–0.004(1)	0.001(1)	–0.002(1)
C(39)	8*f*	0.2759(1)	1.0424(2)	0.1556(2)	0.034(2)	0.025(2)	0.024(2)	–0.003(1)	0.003(1)	–0.004(1)

References

1. Wang, L.-Y.; Zheng, X.-J.; Jin L.-P.; Lu, S. Z.: Crystal structure and HRS study of Eu_2(3,4-DMBA)$_6$(PHEN)$_2$. Chem. J. Chin. Univ. **20** (1999) 110-114.
2. Wang, R.-F.; Wang, S.-P.; Shi, S.-K.; Zhang, J.-J.: Crystal structure and properties of terbium *o*-methylbenzoate complex with 1,10-phenanthroline, [Tb(*o*-$CH_3C_6H_4COO)_3(C_{12}H_8N_2)]_2$. Rare Met. **23** (2004) 103-108.
3. Li, X.; Zhang, Z.-Y.; Wang D.-Y.; Song, H.-B.; Zou, Y.-Q.: Dimeric hexakis(4-methylbenzoato)bis(1,10-phenanthroline)didysprosium(III). Acta Crystallogr. C**61** (2005) m81-m83.
4. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
5. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.